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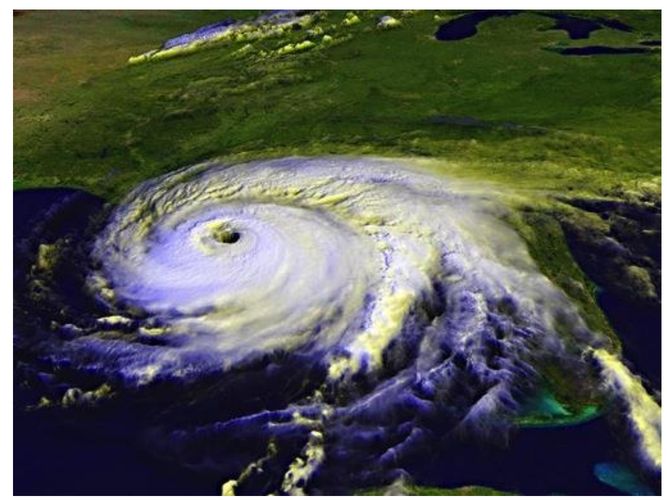

Advanced Materials for Multi-Electron Redox Flow Batteries

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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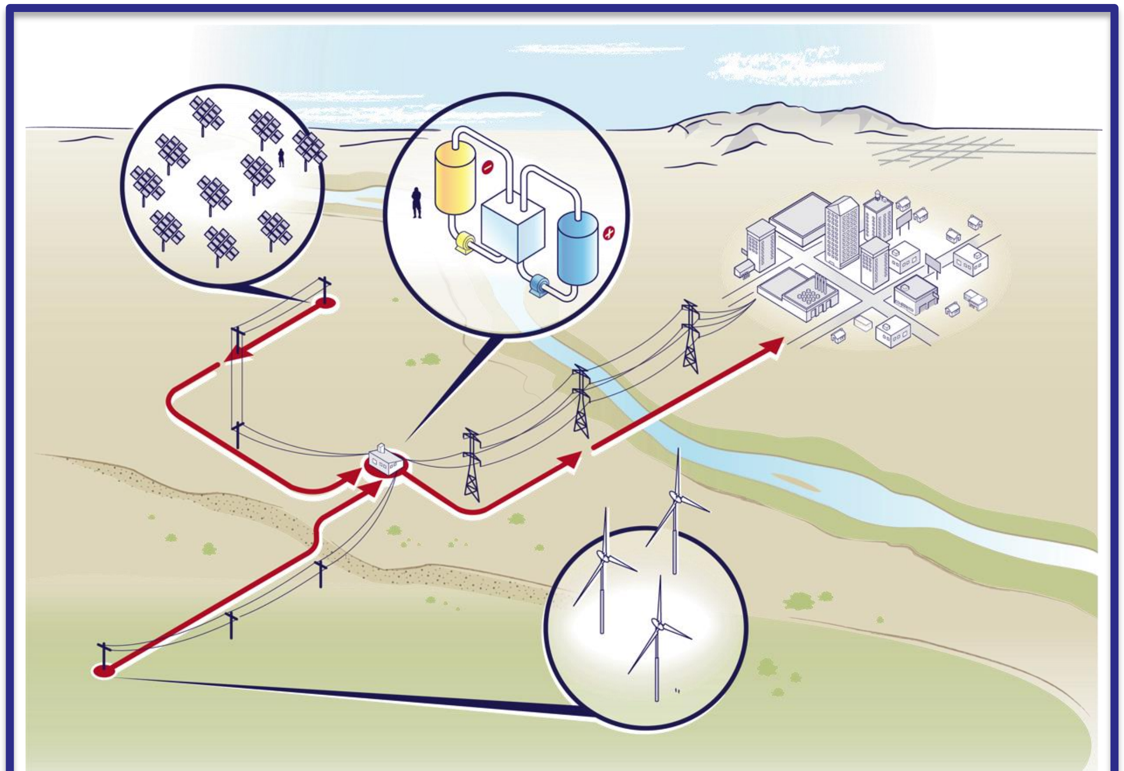
Project Overview

Problem: Cost competitive ionic liquids have high viscosities but are promising for higher energy density redox flow batteries due to higher metal concentrations and wider voltage windows.

Approach: Couple earth-abundant electrolytes with commercial and custom membranes and rapidly test and tune in an iterative fashion using laboratory-scale cell designs.



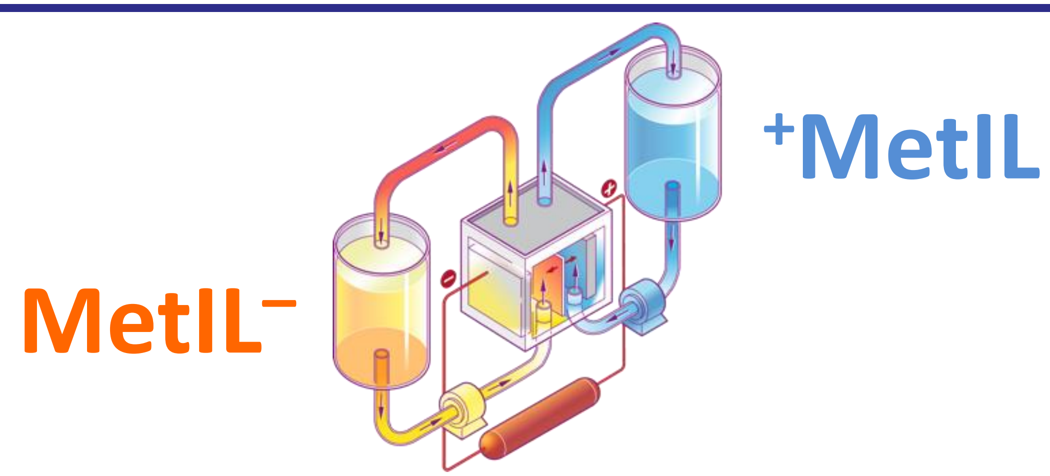
Increased renewables penetration on the grid

$$\textbf{Energy Density}_{RFB} \approx \tfrac{1}{2} nFV_{cell}c_{active}$$

$$ED_{AQ} = \tfrac{1}{2}1F1.5_{cell}2_{active} = \mathbf{1.5F}$$

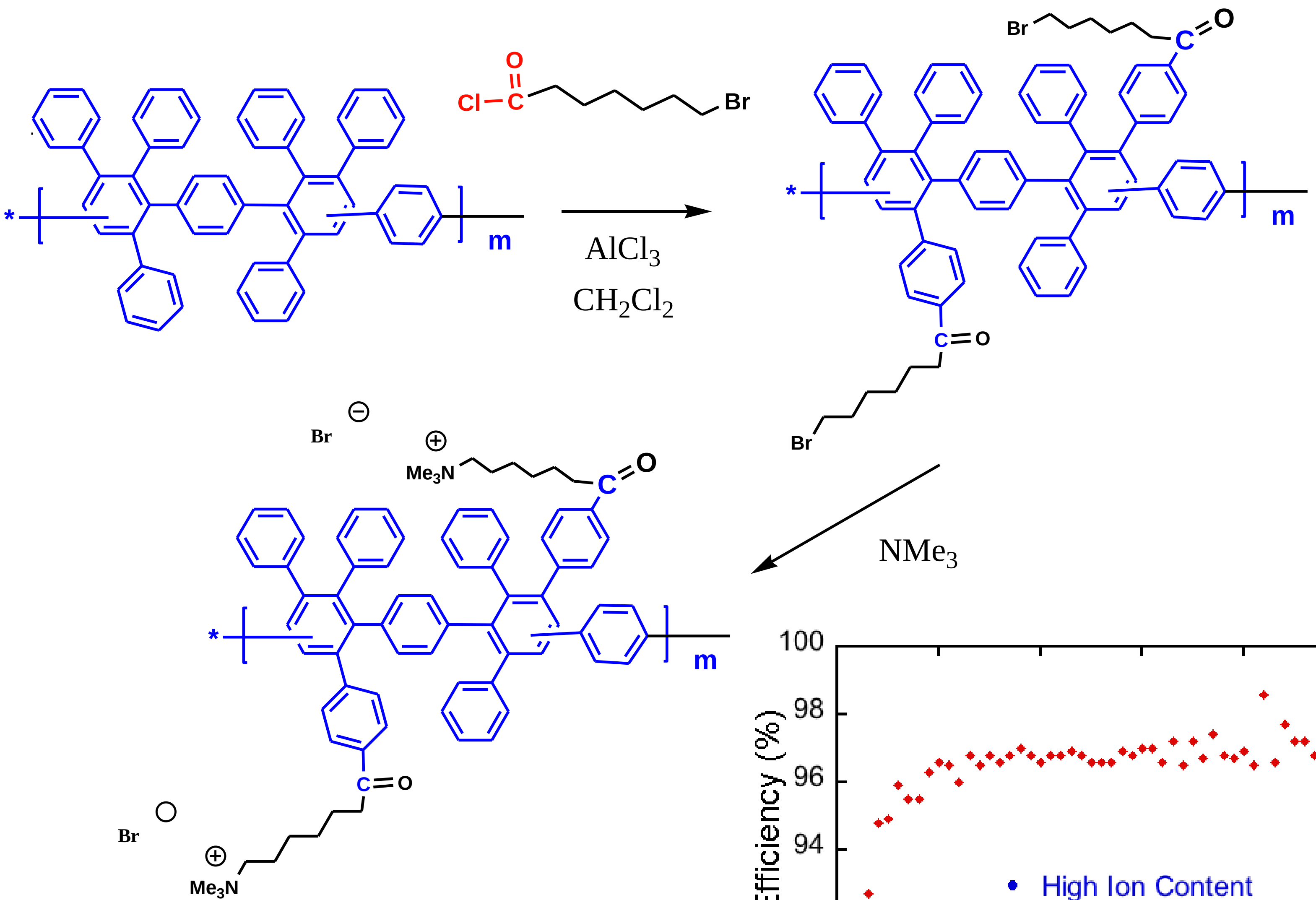
$$ED_{IL} = \tfrac{1}{2}2F2_{cell}3_{active} = \mathbf{6.0F}$$

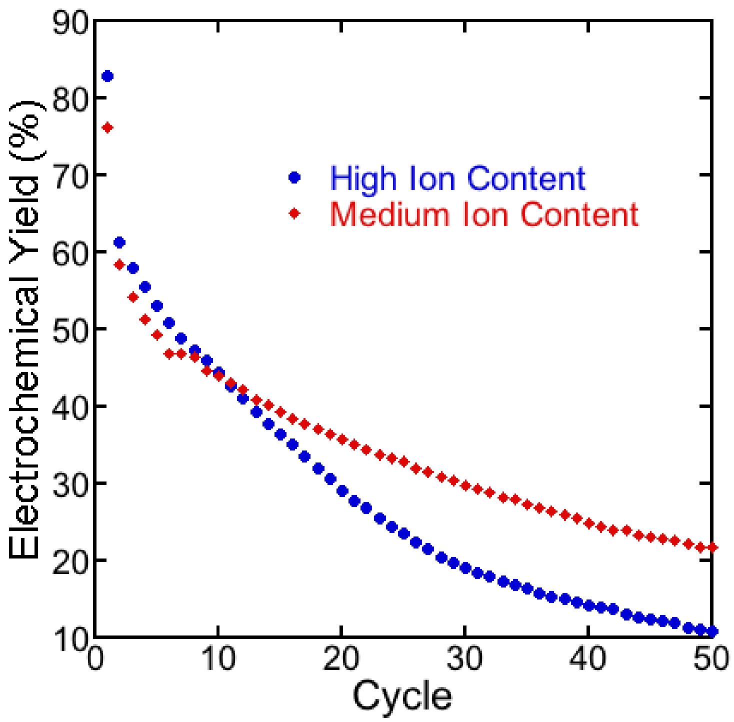
Potential for **four-fold** improvement

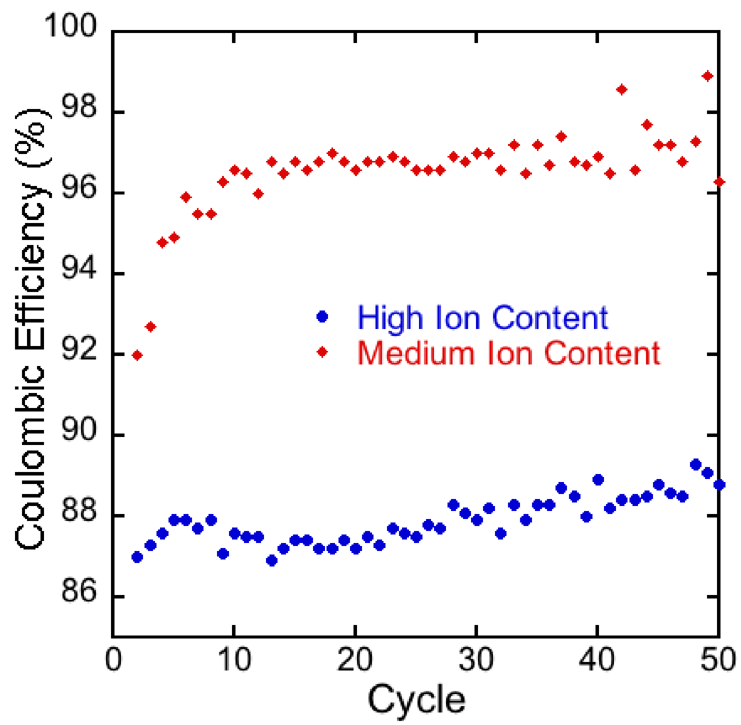


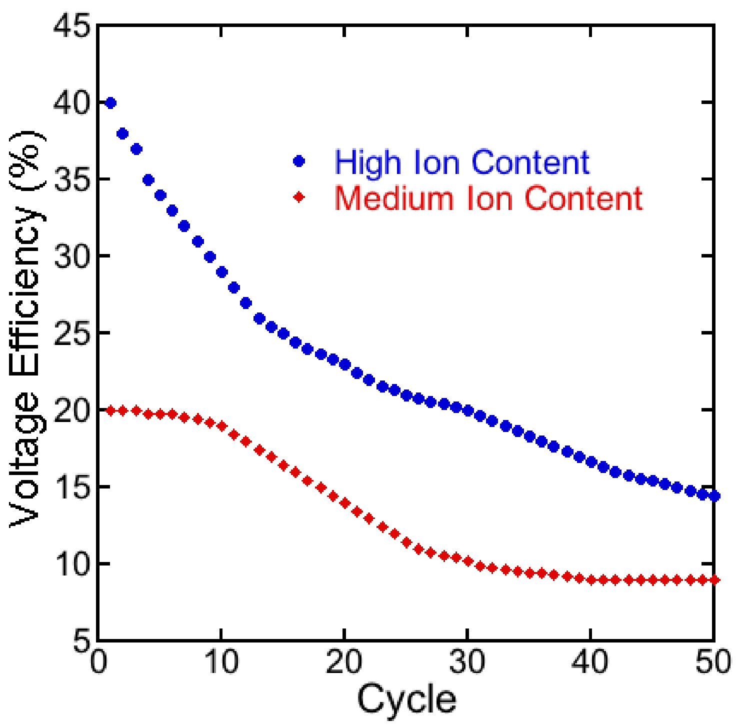
Membrane Ion Content

Membranes contain a polyphenylene backbone with pendant ionic groups; ionic content was varied qualitatively high, medium, and low.









Small, Pratt, Fujimoto, and Anderson, *J. Electrochem. Soc.*, **2016**, A5106.

Post Cycling Studies

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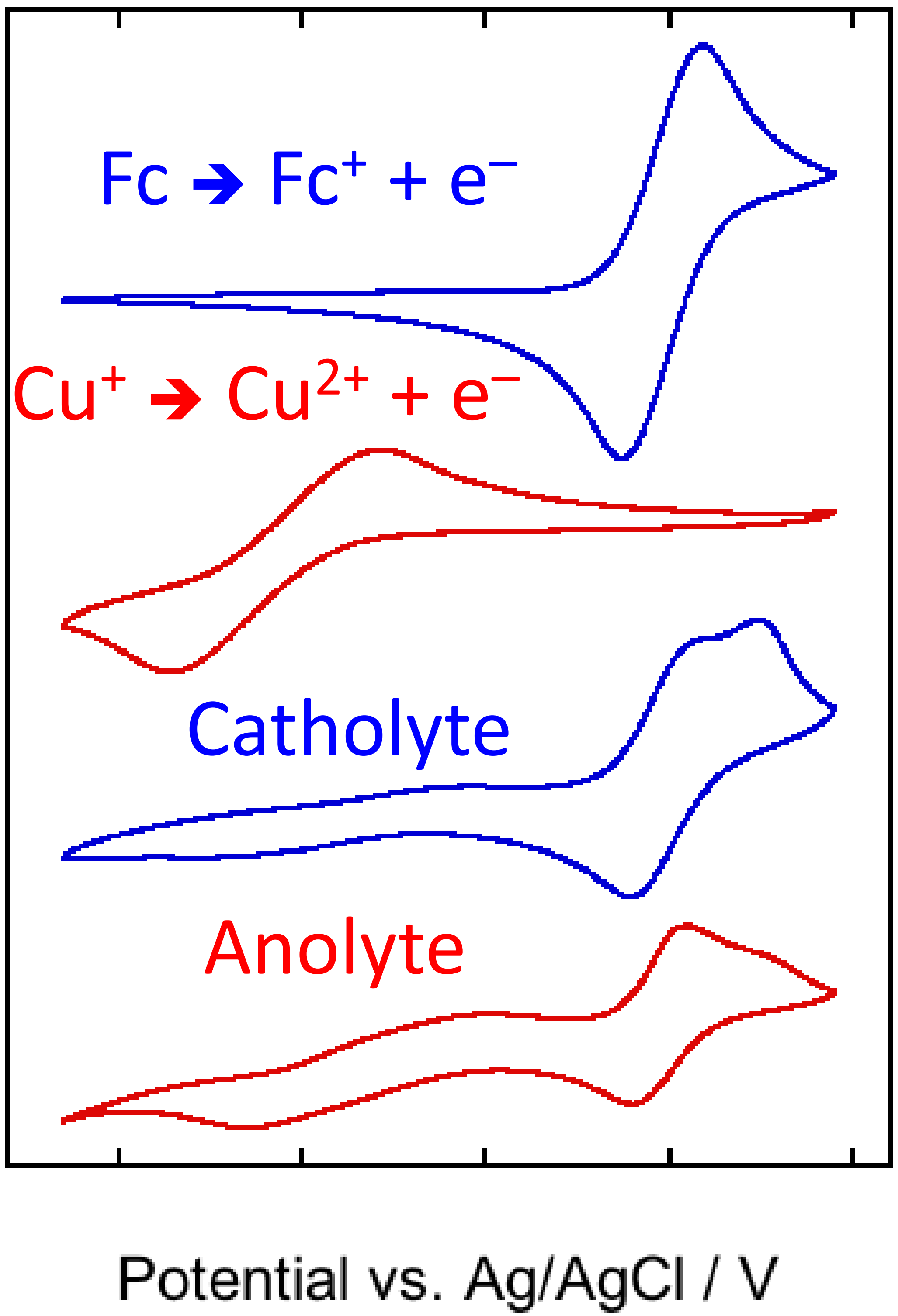
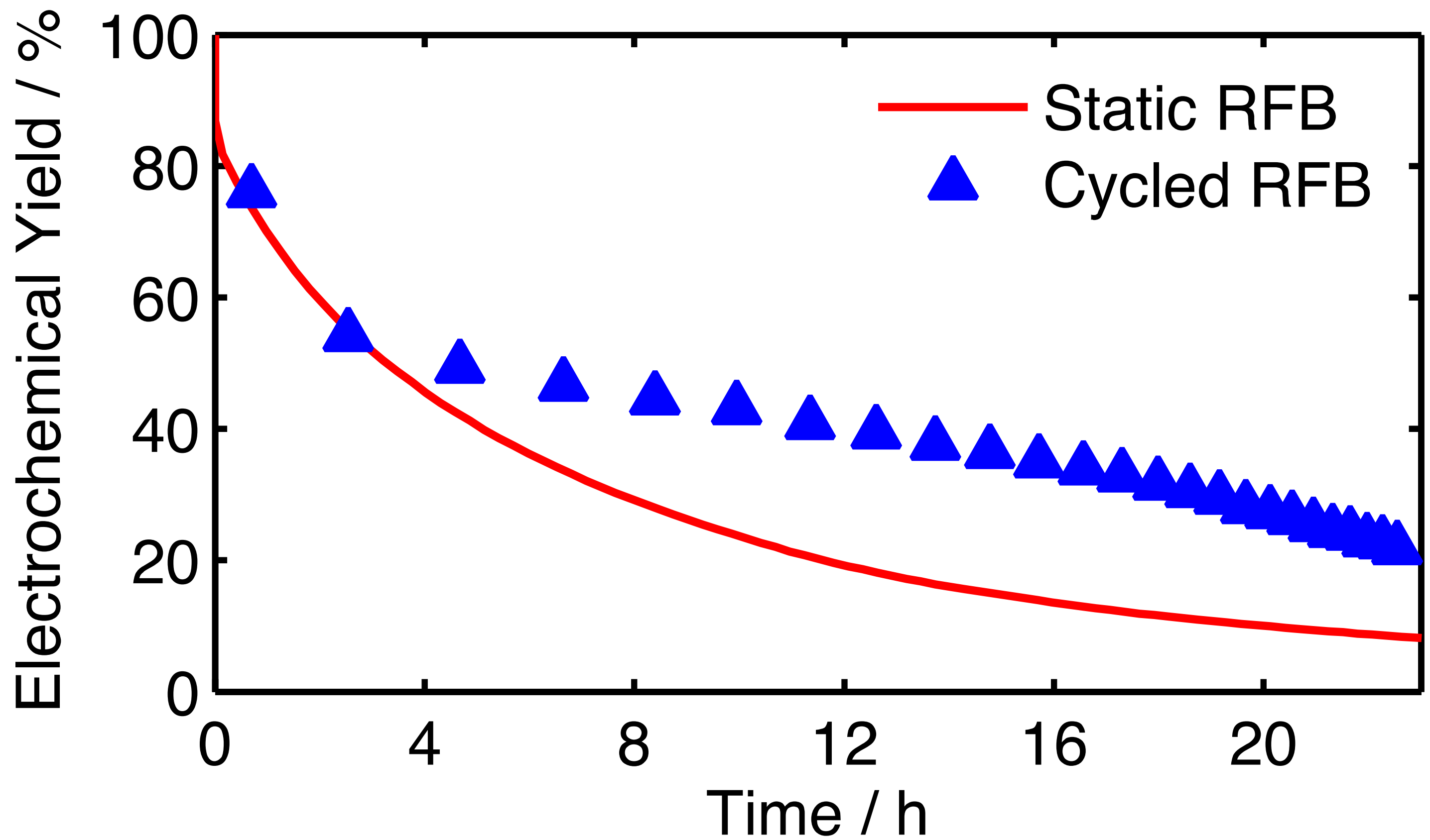
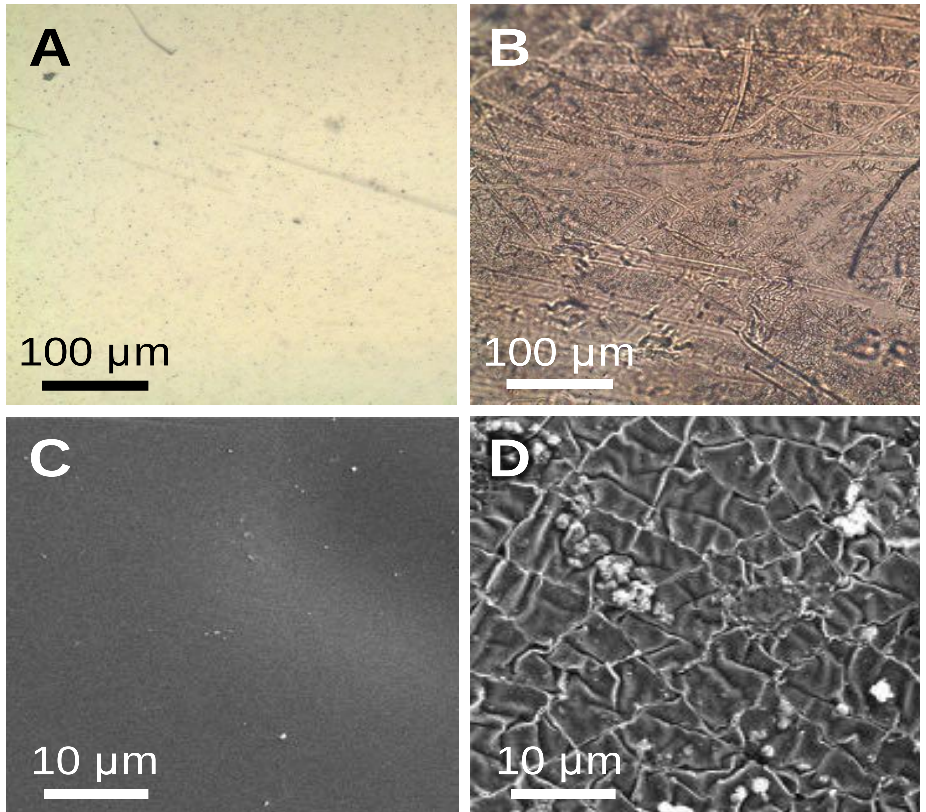




- The decreased electrochemical yield was investigated by (1) cycling rate effects; (2) crossover measurements; (3) impedance; (4) membrane stability.
- The CV as well as the overlay of the static and cycled data show that crossover was responsible for the lowered yield.

Small, Pratt, Fujimoto, and Anderson, *J. Electrochem. Soc.*, **2016**, A5106.

Chemical Stability



Before Cycling **After Cycling**

- SEM and EDS data suggest that there was some decomposition of the ionic liquid.
- The increased resistance after cycling is attributed to the formation of a film on the surface of the membrane.

Membrane Before Cycling

Membrane After Cycling

Supporting Electrolyte

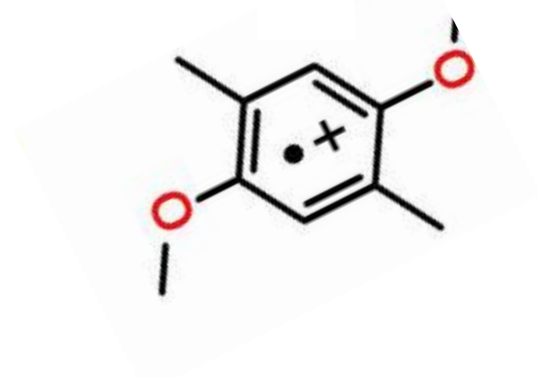
Infrared data shows membrane is stable.

Small, Pratt, Fujimoto, and Anderson, *J. Electrochem. Soc.*, **2016**, A5106.

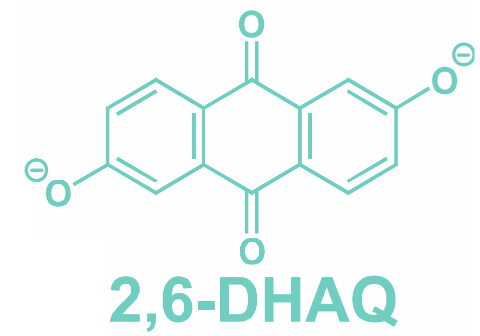
Increasing Energy Density

Recently a number of groundbreaking solutions to higher energy density have appeared.

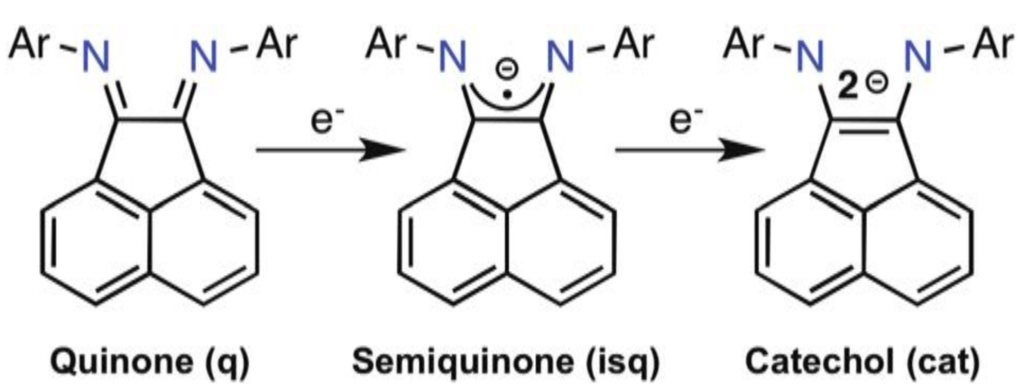
"Lightest Organic Radical Cation…"
Huang, Wang, et. al, *Science Reports,* 2016



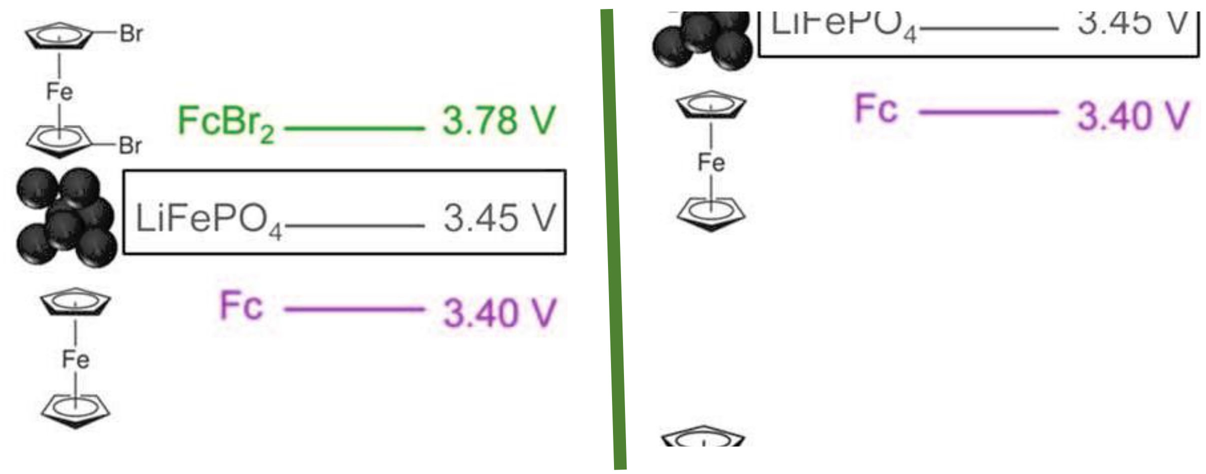
"Alkaline Quinone Flow Battery"
Lin, Aziz, et. al, *Science,* 2016



"Voltage Clustering in Redox-Active Ligands…"
Zarkesh, Anstey, et. al, *Dalton Trans.,* 2016



"High-energy density non-aqueous …"
Jia et. al, *Science Adv.,* 2016



Hybrid Nafion-PVDF Li-conducting membrane

Can we make the solvent and supporting electrolyte "filler" electrochemically active?

Increasing Energy Density–Strategy

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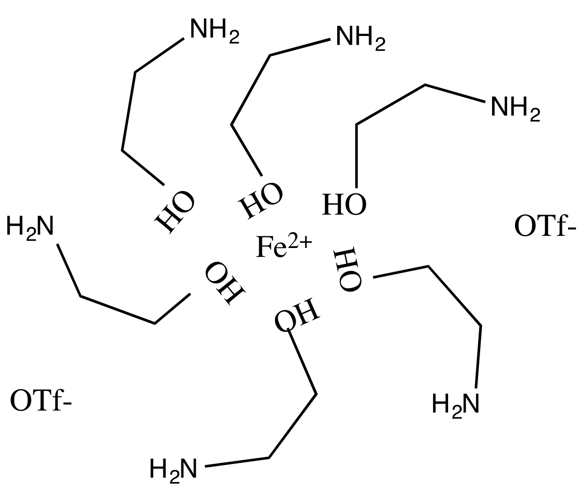
Start with Sandia's MetILs and replace increasing amounts of "filler" with redox active compounds (I^-, Fc) until it becomes impractical.



Replace 1st OTf^- with redox-active I^- →

Single liquid phase at 25 °C

Replace 2nd OTf^- with redox-active I^- →

Phase separation

Couple FcCOOH to 1st ligand ↓

T_{melt} ~70 °C →

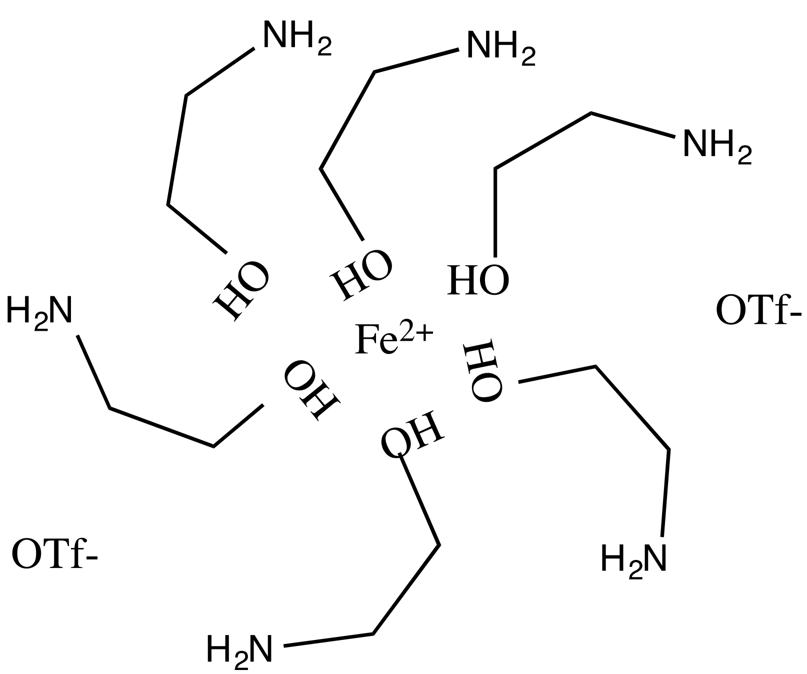
T_{melt} ~60 °C Single liquid phase

Couple FcCOOH to 2nd ligand ↓

T_{melt} >100 °C

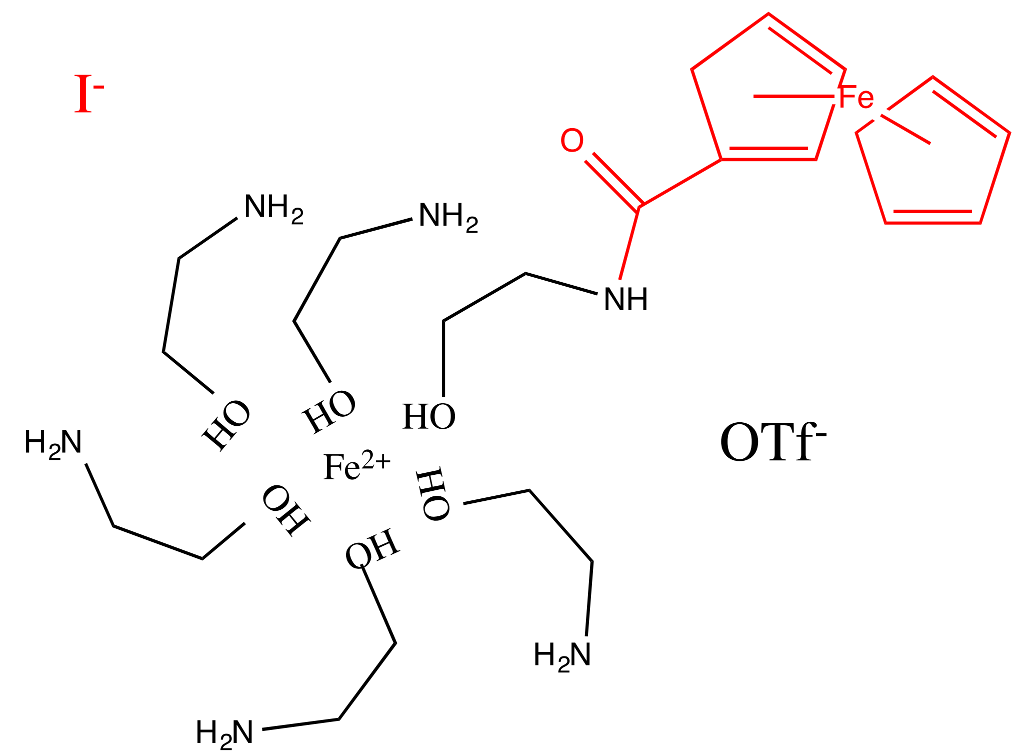
MetILs[3]

Fe-MetIL



Redox activity added to the ligands and anions

Fe-MetIL[3]



2.8 M redox-active e$^-$ → **7.4 M redox-active e$^-$**

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

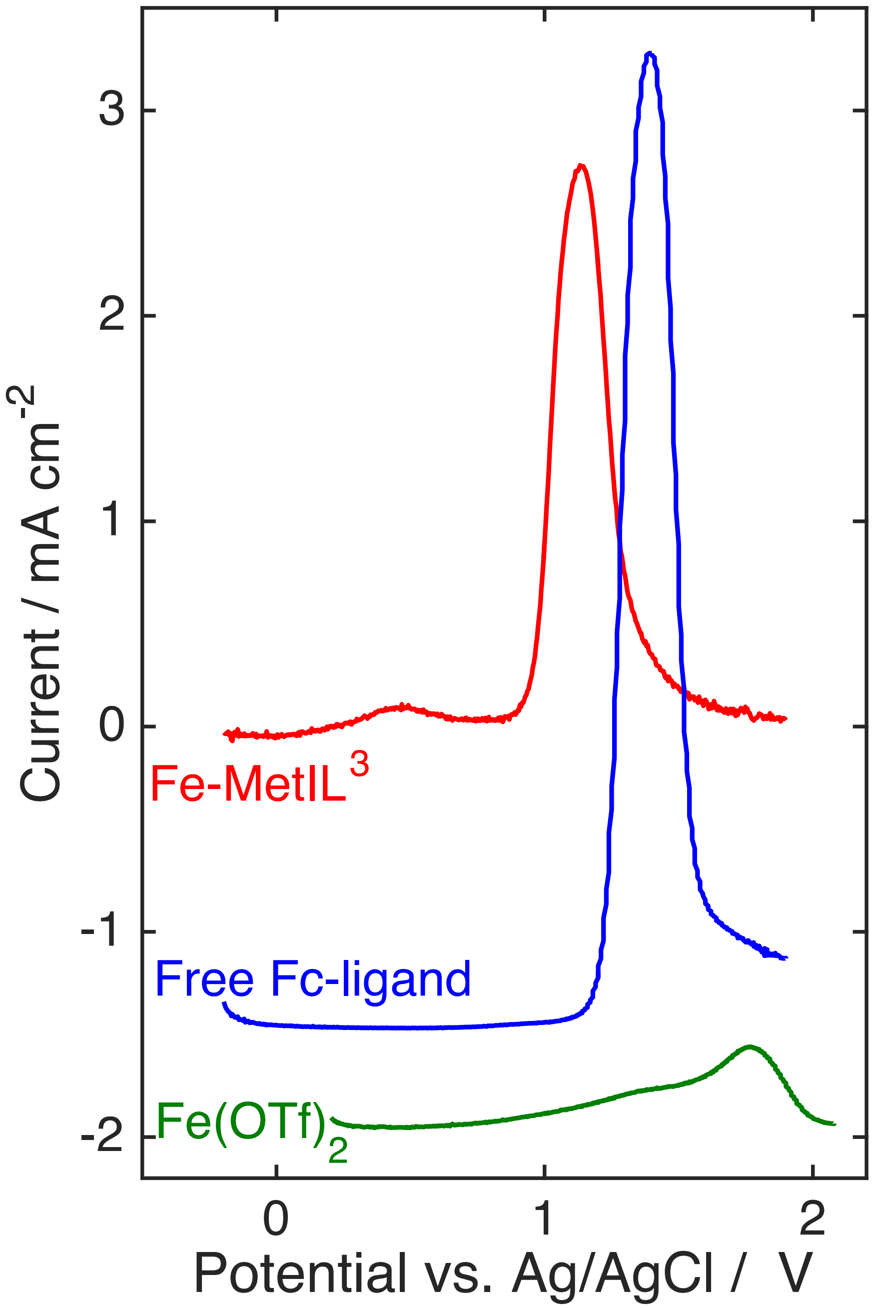
$Fe^{2+} \rightarrow Fe^{3+} + e^-$

$Fc \rightarrow Fc^+ + e^-$

$3I^- \rightarrow I_3^- + 2e^-$

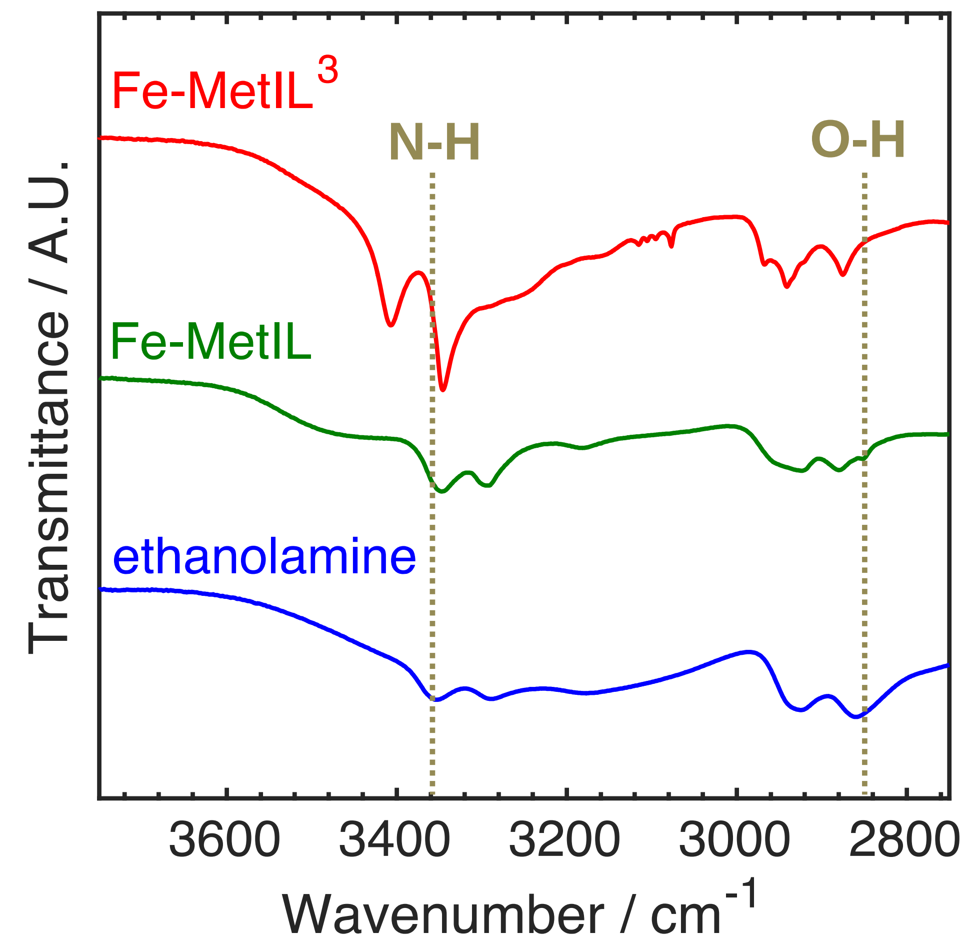
MetILs^3 Characterization

Square Wave Voltammetry



Fe^{2+} and Fc-ligand shift to lower potentials when MetIL forms

Infrared Spectroscopy



Ethanolamine Peak	3354 (N-H)	2860 (O-H)
Fe-MetIL	7	20
Fe-MetIL^3	8	15

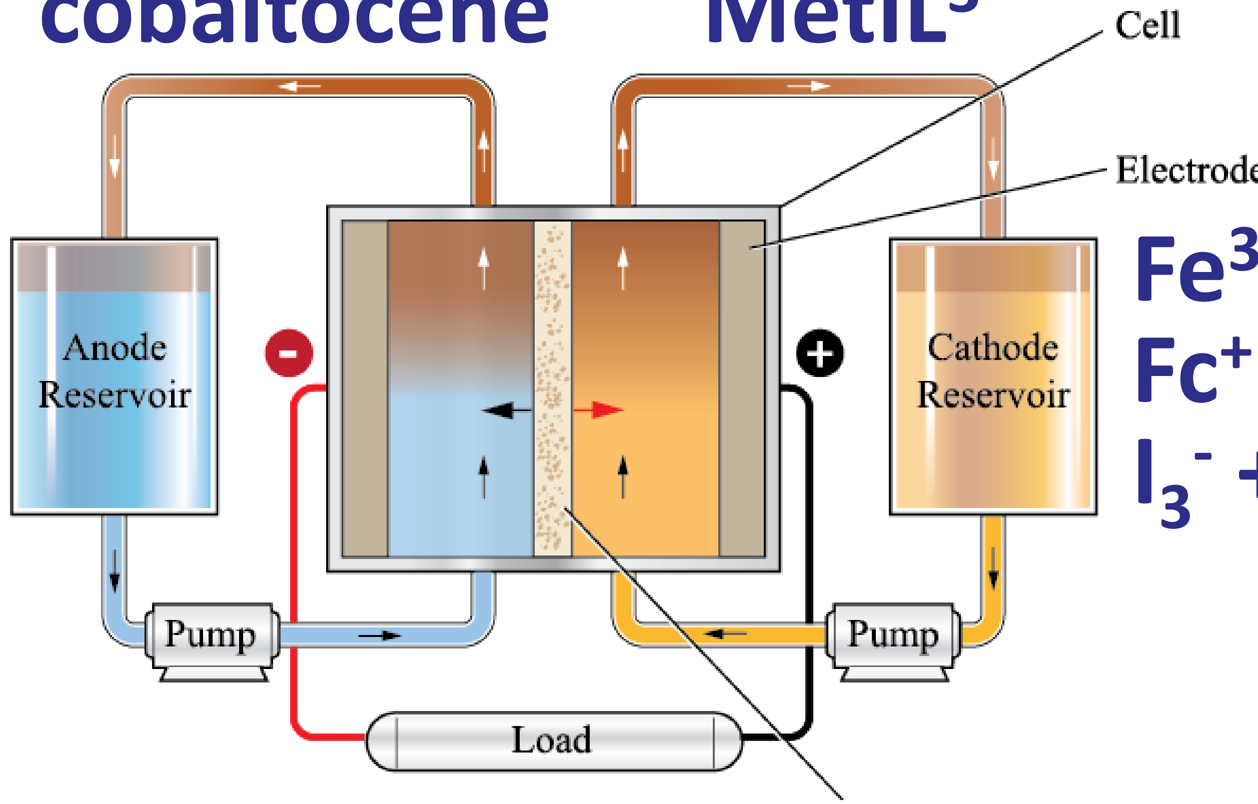
Ethanolamine O-H and N-H IR peaks shift upon complexation

MetILs³ Initial Flow Cell Studies

cobaltocene MetIL³

$Cc \rightarrow Cc^{+} + e^{-}$

200 mM
0.5 M $LiNTf_2$ in PC
5 mA/cm^2

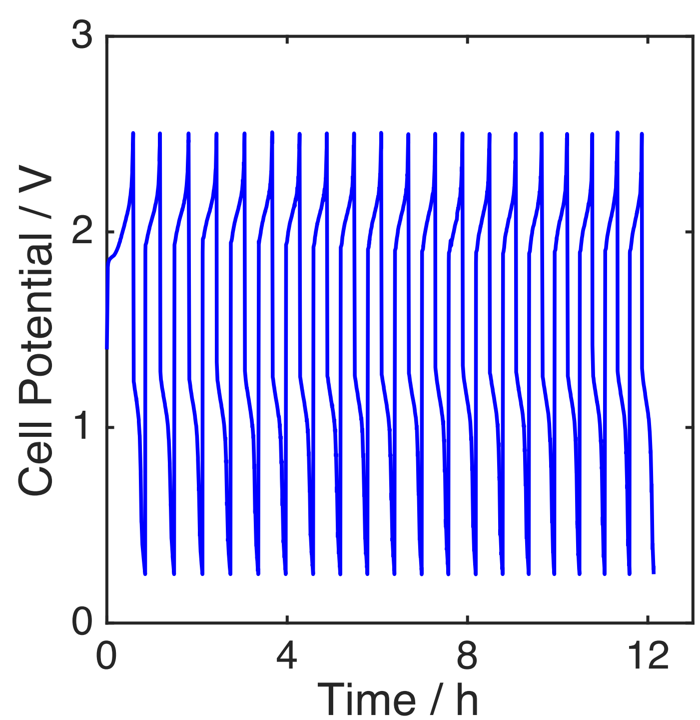


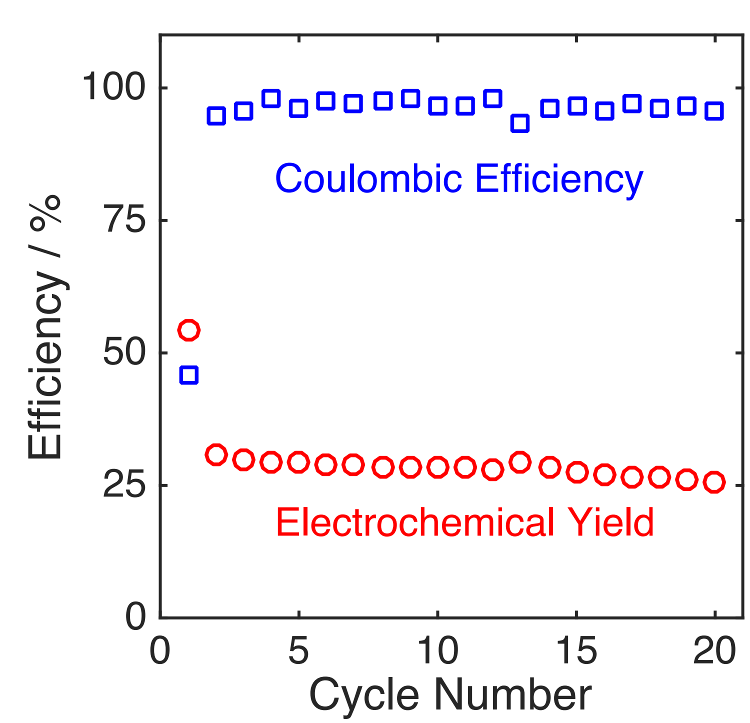
$Fe^{3+} + e^{-} \rightarrow Fe^{3+}$
$Fc^{+} + e^{-} \rightarrow Fc$
$I_3^{-} + 2e^{-} \rightarrow 3I^{-}$

100 mM
0.5 M $LiNTf_2$ in PC
5 mA/cm^2

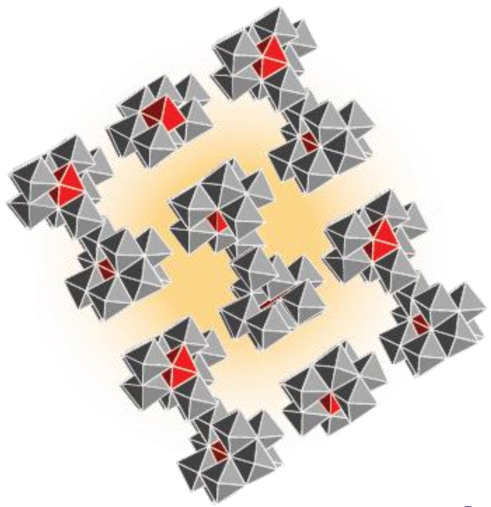
Membrane: Fumasep FAP-PK (anion exchange)

Cell shows good cyclability after initial capacity loss.



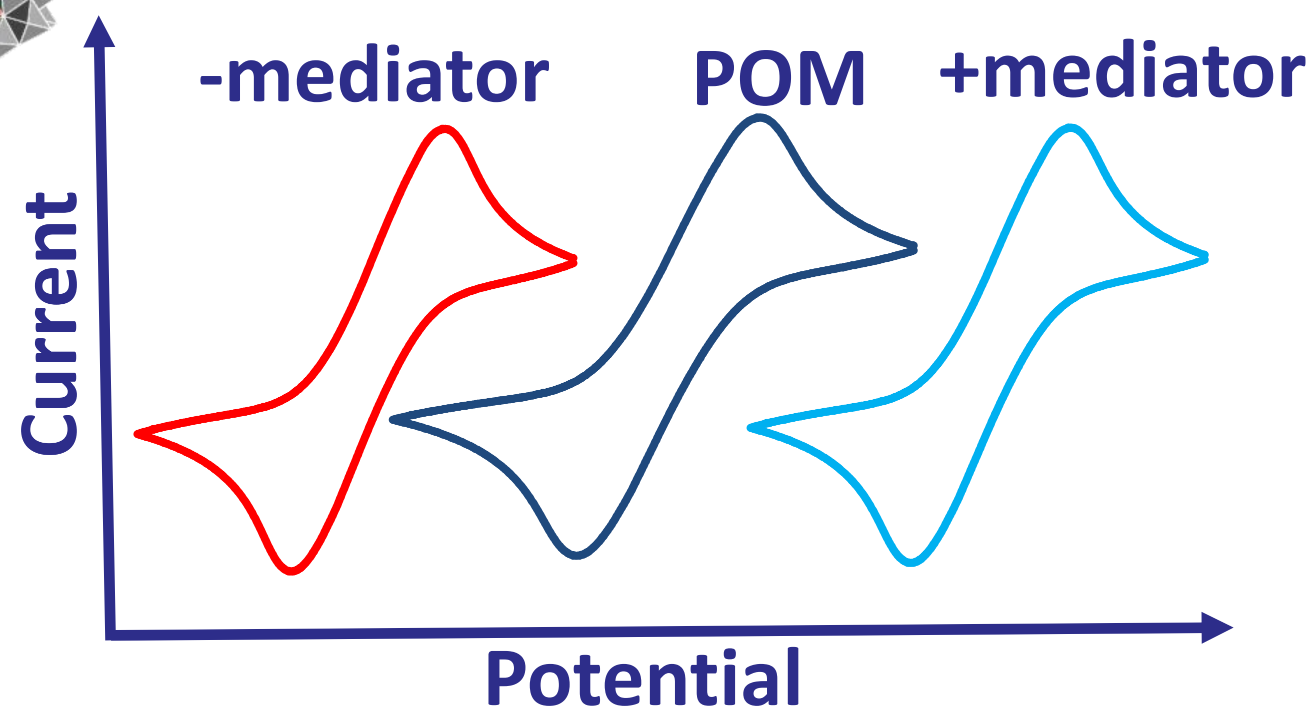


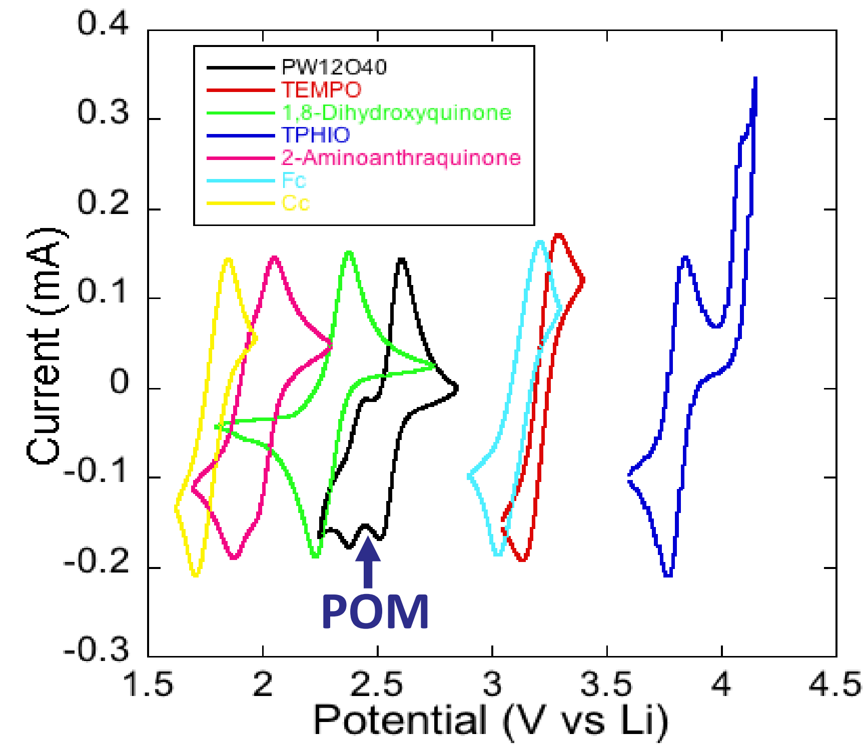
Mediated Flow Batteries

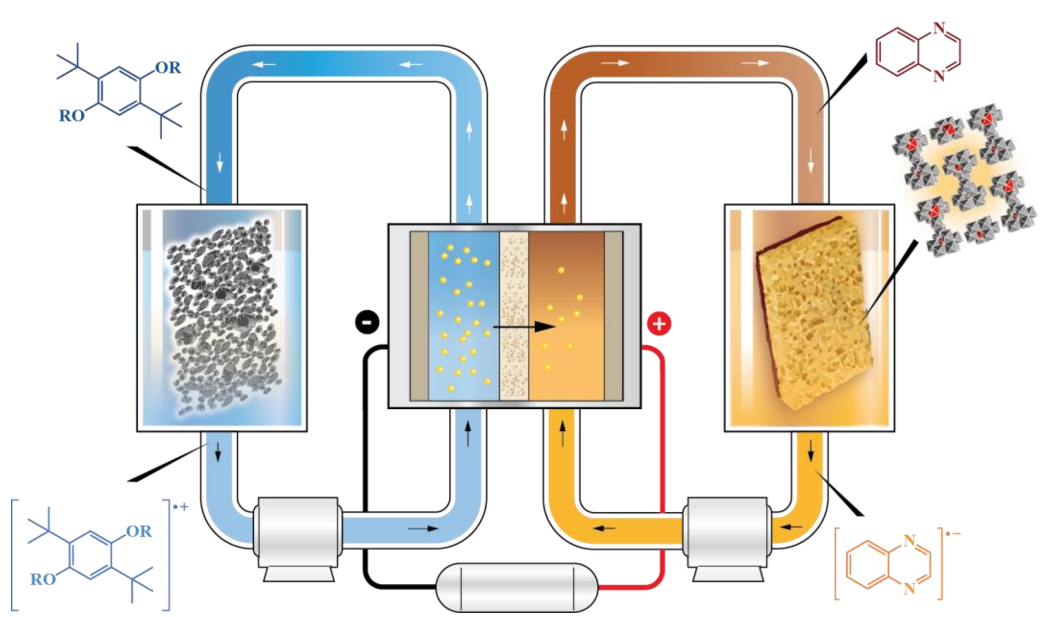


Polyoxometalate (POM) cathode: $Na_3PW_{12}O_{40}$

$$PW_{12}O_{40}^{3-} + 24e^- \rightarrow PW_{12}O_{40}^{27-}$$







- energy stored in easily exchangeable canisters of material
- mediators serve as redox shuttles between electrodes and canisters
- polyoxometalates may be substituted with traditional lithium intercalation materials

Summary and Acknowledgements

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- Diels Alder polyphenylene membranes with tunable ion content provide an alternative to commercial systems.
- MetILs^3 utilizes electrolyte “filler” to increase theoretical energy density 3X from 190 to 620 Wh/L over MetILs.
- In 2016 the team published two new papers including one featured on the cover of *Journal of Materials Chemistry A* and was granted one new patent.

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